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Original Article

Synthesis of Zinc(II)2-(quinolin-8-yl)benzoate dehydrate metal organic framework and its luminescence activity

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ABSTRACT

Synthesis and characterization of zinc(II)2-(quinolin-8-yl)benzoate dehydrate is presented in this research work. This new complex was obtained by reacting quinolin-8-yl-benzoate with zinc sulfate heptahydrate. The characterization was done by ultraviolet (UV)–visible spectroscopy (UV–Vis), elemental analysis, Fourier transform infrared (FTIR), scanning electron microscope, nuclear magnetic resonance (^{1}H-NMR), and powder X-ray diffraction spectroscopy. FT-IR and UV–visible spectrum of the complex establishes a monodentate mode of coordination in the 8-hydroxyquinoline and benzoic acid, respectively. Tetrahedral structure was proposed for this complex compound. Result from the luminescence studies and its surface analysis shows that this complex is a potential material for light emitting diodes because of its strong absorption in the UV region.

Keywords: Light emitting diodes, metal organic framework, photoluminescence

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INTRODUCTION

The rate of population increase and the usage of fossil fuels have given rise to the need for alternative and sustainable energy development. There is, therefore, a need for energy saving materials that are affordable and that pose no threat to our environment. Areas of interests such as fuel cells, batteries, capacitors, and solar cells afford much opportunity for improvement and research focus.[1-3] Luminescent metal organic frameworks (MOFs) are potentially useful as chemically selective sensors. The study of luminescence behavior in MOFs is an active area of research in physics and inorganic chemistry.[3-16] A large number of 3d elements have been employed to investigate their luminescence. The most commonly reported MOF structures are based on Zn^{2+} and Cd^{2+} ions, which have filled d orbital and thus d–d transitions, are not possible. In these compounds, intraligand and/or ligand metal charge transfer effects have been observed.[11] The photoluminescence study is important to understand the charge transfer pathways.[8] The studies on the luminescence behavior in MOFs clearly indicate that the energy transfer from the organic ligands to the metal center is easy. The lifetime studies also suggest that the excited state possess considerable stability and allows for exploitation in many important applications.[17-21]

MATERIALS AND METHODS

All chemicals used in synthesis were purchased commercially from Sigma-Aldrich Company and were used without further purification. The infrared (IR) spectrum of the complex was taken on a (Shimadzu, Fourier transform IR [FTIR]-8400S) FTIR spectrophotometer (4000-400 cm^{-1}) with sample prepared as KBr discs. The electronic spectrum was measured in the range of 200–700 nm at room temperature with M501 single beam ultraviolet (UV)–visible spectrophotometer. The image of the complex was taken in a magnification range of 300-80 µm using a Joel JEM-5200 operating at an acceleration voltage of 20 kV. The powder X-ray diffraction pattern for the complex was collected using a PAN analytical X'PERT pro automatic diffractometer operating at 40 kV and 30 mA.

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Synthesis Zinc(II)2-(quinolin-8-yl)benzoate dehydrate

The Zn(II) complex was synthesized with modification to methods reported by Mfor *et al*., 2014. To a 10 ml aqueous solution of $ZnSO_4.7H_2O$ (2.874 g) was added in drop with constant stirring at 25°C quinolin-8-yl-benzoate (3.00 g) in 20 ml methanol. The solution was further stirred for 3 h. Plate-like crystals formed within 5 days were washed and stored in vacuo. Figure 1 shows the synthetic scheme of Zn(II) metal organic frame work at 25°C.

RESULTS AND DISCUSSION

Combination of quinolin-8-yl- benzoate and zinc sulfate heptahydrate in a solvent system of methanol/water at 25°C temperature yielded colorless polycrystals of $Zn(C_{16}H_{11}NO_2)2.2H_2O$. The solubility of the ligand and metal complex was determined in some organic solvents. The synthesized compound showed solubility only in strong coordinating solvents such DMSO. The powder X-ray analysis of the Zn(II) complex revealed that the compound is highly crystalline. The elemental analysis in Table 1 shows that the pH value and conductivity for the complex are acidic and non-electrolytic nature, respectively.

^{1}H-NMR Spectrum

The ‘H-NMR spectrum of Zn(II)2-(quinolin-8-yl)benzoate dehydrate [Figure 2] was recorded in DMSO [Table 2]. The observed signals in the spectrum were assigned to the synthesized compound. The peaks observed at δ value, 8.83–8.02 ppm were assigned to the quinolin-8-ylbenzoate protons in the molecule. The signals observed in the range of 7.50–6.84 ppm were assigned to the different types of aromatic protons in the Zn(II)2-(quinolin-8-yl)benzoate dehydrate moieties. The singlet peak at 7.60 ppm was assigned to the methylene protons of the quinolin-8-ylbenzoate in the compound moiety. The inductive effect of the two oxygen atoms deshielded the methylene protons and this resulted in the higher δ value for these protons. The peak in the range of 7.60–7.68 ppm was assigned to the -C =O protons from the ligand moiety. The steric effects of the nitrogen atoms within the ligand are suggested to be responsible for the high value.

UV Spectrum

The UV spectrum of the compound is shown in Figure 3. The Zn(II) complex reveals a broadband and λ_{max} at 231 cm^{-1} considered to be charge transfer transitions. The bands show that the complex absorbed in the UV region, thereby making it

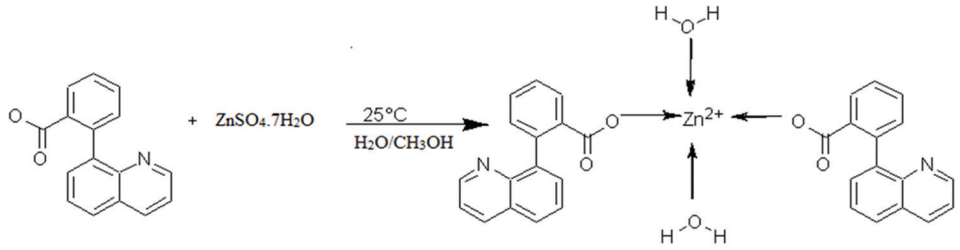

Figure 1: Zinc(II)2-(quinolin-8-yl)benzoate dehydrate

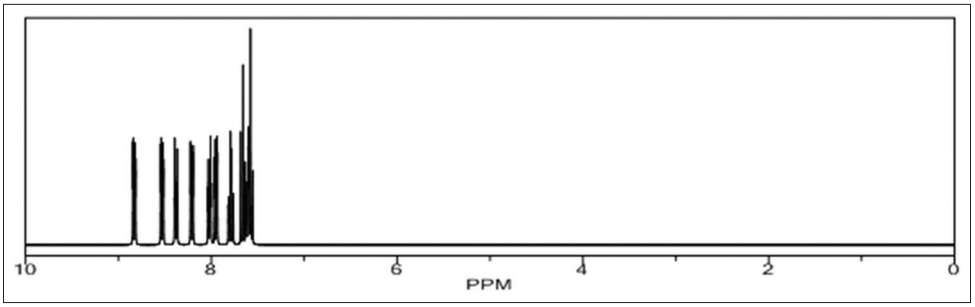

Figure 2: ^{1}H-NMR spectrum of zinc(II)2-(quinolin-8-yl)benzoate dehydrate

Table 1: Analytical and some physical properties of Zn(II) complex and its ligands

Compound	Physical state	Melting point°C	% Yield	(Ω^{-1} cm^2 mol^{-1})	pH	%found (Calc.)				
						C	H	N	O	M
$C_{16}H_{11}NO_2$	Crystalline	95–97	79.6	1.24	2.55	77.10 (77.30)	4.45 (4.42)	5.62 (5.53)	12.83 (12.75)	
$C_{32}H_{24}N_2O_6Zn$	Crystalline	100–102	79.6	1.24	2.80	64.28 (64.30)	4.05 (4.03)	4.69 (4.72)	16.05 (15.75)	10.93 (10.97)

M/Z: 596 (100%), 598 (64.8%), 600 (46.0%), 597 (35.9), 599 (30.1%), 601 (15.1), 602 (4.3%)

Table 2: Significant 1H-NMR peaks assignments of zinc(II)2-(quinolin-8-yl)benzoate dehydrate

Chemical shifts (δ ppm)	Proton assignments
8.02 m 7.95 s	Four -CH2-
8.83–8.53 m	Six H-C*CH*C-H (H-C*CH)
7.58 m 8.79–7.60 m	Aromatic protons

*S: Singlet, m: Multiplet

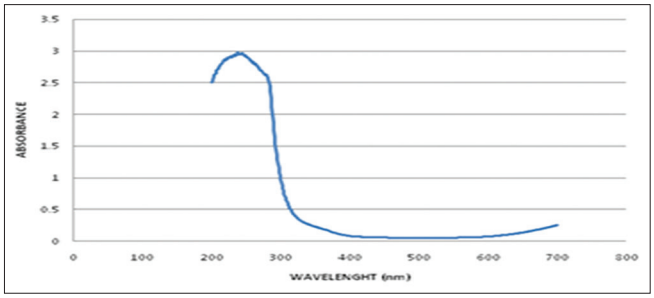

Figure 3: Ultraviolet–visible spectrum of the Zn(II) complex

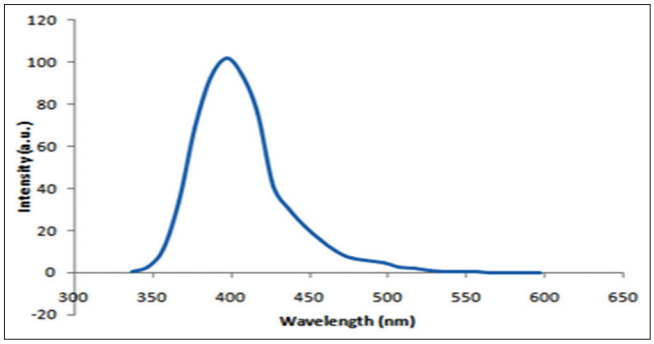

Figure 4: Fluorescence emission spectrum of Zn(II) complex

capable of absorbing energy, having a light photoluminescent property.[10]

Fluorescence Emission Spectrum

A 3.12 electron volt (eV) corresponding to a wavelength of approximately 400 nm implies that Zn(II) complex [Figure 4] can be used as a semiconductor device and has the potential of being readily activated by thermal energy. The 3.12 (eV) is an indication that the synthesized Zn(II) complex has a wide-bandgap which can allow it operate at higher temperatures on the order of about 300°C making it attractive in military application.[19-21]

INFRARED SPECTRUM

The IR spectrum of the Zn(II) complex [Figure 5] exhibited bands with the appropriate shifts due to complex formation. The following vibration bands were observed at 3463.30,

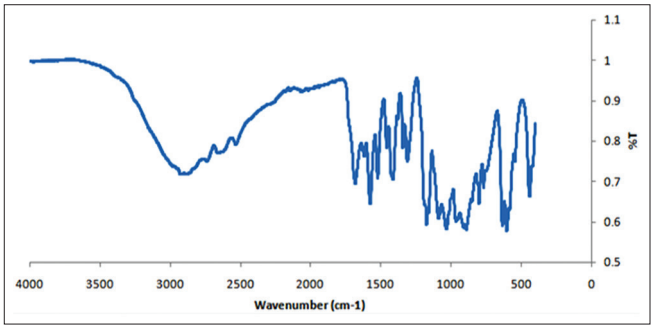

Figure 5: Fourier transform infrared spectrum of the Zn(II) complex

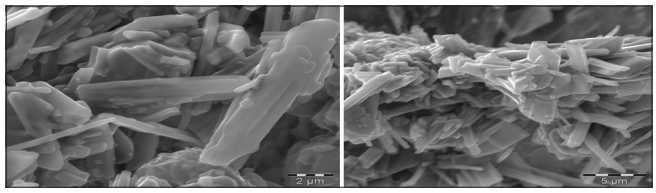

Figure 6: Scanning electron microscope image of Zinc(II)2-(quinolin-8-yl)benzoate dihydrate

3064.03, 1618.33, 1407.12, and 1004.95 assigned to υ(O-H), $\upsilon(CH_2)$, υ(C=C), $\upsilon(CH_4)$, and υ(C-H), respectively.[5,11,13]

Scanning Electron Microscope (SEM) Images

The SEM images of the Zn(II) MOFs are shown in Figure 6. It can be seen that plate-like crystal shape is observed, most probably due to the polycrystalline agglomerate nature of the crystals.[2]

Powder X-ray Diffractometer (PXRD) Patterns

The peaks in the PXRD patterns of the Zn(II) complex in Figure 7 show that the compound is crystalline in nature and in good agreement with the simulated pattern. The crystallite size D, for the complex (23.45 nm), was estimated from the Scherer's equation:[14]

$$D = \frac{k\lambda}{\beta cos\theta}$$

Where, D is the crystallite size, $k = 0.9$ which is a correction factor to account for particle shape, β is the full width at half maximum of the most intense diffraction peak, $\lambda = 1.5406$ Å of the Zn target, and θ is the Bragg angle.

CONCLUSION

A photoluminescent MOF of Zn(II) has been synthesized and characterized by SEM, infrared spectroscopy, fluorescence and UV–visible spectroscopy, and other physical properties. The crystal lattice structure of the framework has been well demonstrated by PXRD patterns of the compound. UV and photoluminescence were studied for the compound at room

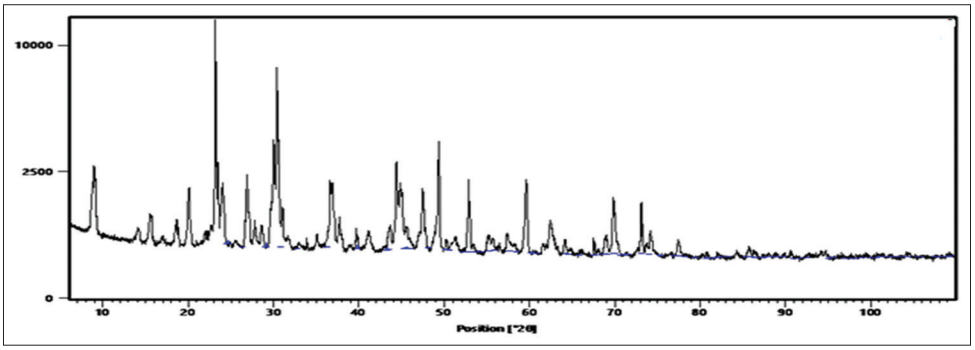

Figure 7: Powder X-ray diffractometer diffraction pattern of Zn(II)2-(quinolin-8-yl)benzoate dehydrate

temperature. Tetrahedral structure was proposed for the Zn(II) complex based on the electron microscope and UV–visible spectrum studies. The photoluminescence property of the compound might be very useful for chemically selective sensors, solar cells, capacitors, batteries, and a wide range of applications.

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AUTHORS' CONTRIBUTIONS

The two authors contributed to the conception, design, material preparation, and data collection for this study. The analyses were performed by Idongesit Justina Mbonu and Charles Chisom Mbonu.

The first draft of the manuscript was written by Charles Chisom Mbonu and all the authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Idongesit Justina Mbonu and Charles Chisom Mbonu. The first draft of the manuscript was written by Charles Chisom Mbonu and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Conceptualization: Idongesit Justina Mbonu; methodology: Idongesit Justina Mbonu; formal analysis and investigation: Charles Chisom Mbonu; writing – original draft preparation: Charles Chisom Mbonu; writing – review and editing: Idongesit Justina Mbonu; funding acquisition: Idongesit Justina Mbonu and Charles Chisom Mbonu; and supervision: Idongesit Justina Mbonu.

CONFLICTS OF INTEREST

The authors declared that they have no conflicts of interest.

REFERENCES

1. Zang J, Johnson J. Porous Materials-metal-organic Framework. United States: Nanocamp, NCMN, UNL; 2012. p. 1-30.
2. Zhao D, Timmons DJ, Yuan D, Zhou H. Turning the topology and functionality of metal-organic framework by ligand design. Acc Chem Res 2011;44:123-33.
3. Zhou YH, Tian YP. Synthesis, crystal structure and photoluminescent property of Cd(II) metal-organic framework with mixed carboxylate and bis(imidazole) ligand. Korean Chem Soc 2013;34:2800-2.
4. Baumann TF. Metal-organic Frameworks: Literature Survey and Recommendation of Potential Sorbent Materials. California, United States: Lawrence Livermore National Laboratory; 2010. p. 3-10.
5. Arunachalam T, Bhakyaraj R, Sasi AK. Synthesis, characterization and biological activity of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes of benzoic acid ligand. E J Chem 2009;6:743-6.
6. Ihara H, Takafuji M, Kuwahara Y. Polymer functionalization by luminescent supramolecular gels. Polym J 2016;48:843-53.
7. Stanley DA, Alizadeh H, Helmy A, Kherani NP, Qian L, Zukotynski S. SEM mapped micro-photoluminescence studies of highly luminescent micro-clusters in erbium-doped silicon-rich silicon oxide. J Lumin 2011;131:72-7.
8. Tella AC, Aaron IY. Synthesis and applications of metal organic frameworks materials: A review. Acta Chim Pharm Indic 2012;2:75-81.
9. Gfroerer TT. Photoluminescence in analysis of surfaces and interfaces. In: Encyclopedia of Analytical Chemistry. United States: John Wiley & Sons, Ltd.; 2000. p. 9209-31.
10. Onal Z, Zengin H, Sonmez M. Synthesis, characterization and photoluminescence properties of Cu(II), Co(II), Ni(II) and Zn(II) complexes of N-aminopyrimidine-2-thione. Turk J Chem Sci 2011;35:905-14.
11. Li A, Tong Y, Cao B, Song H, Li Z, Chen X, *et al*. MOF-derived

multifractal porous carbon with ultrahigh lithium-ion storage performance. Sci Rep 1-8
12. Hu M. Design, Synthesis and Applications of Metal Organic Frameworks, Thesis. Massachusetts: Worcester Polytechnic Institute; 2011. p. 24-34.
13. Fernandez CA, Nune SK, Motkuri RK, Thallapally PK, Wang C, Liu J, *et al*. Synthesis, characterization, and application of metal organic framework nanostructures. Langmuir 2010;26:18591-4.
14. Konar S, Jana A, Das K, Ray S, Chatterjee S, Golen JA, *et al*. Synthesis, crystal structure, spectroscopic and photoluminescence studies of Mn(II), Co(II), Cd(II), Zn(II) and Cu(II) complexes with a pyrazole derived Schiff baseligand. Polyhedron 2011;30:2801-8.
15. Lefebvre J, Manuyama S, Finnie P. Photoluminescence: Science and applications. Carbon Nanotubes Top Appl Phys 2008;111:287-319.
16. Lim SY, Forster M, Zhang X, Holtkamp J, Schubert MC, Cuevas A, *et al*. Applications of photoluminescence imaging to Dopant and carrier concentration measurements of silicon wafers. IEEE J Photovolt 2012;2012:1-7.
17. Lux L, Williams K, Ma S. Heat treatment of metal-organic frameworks for green energy applications. CrystEngComm 2015;17:10-22.
18. Manna B, Singh S, Ghosh SK. Guest driven structure transformation studies of a luminescent metal organic framework. Indian Acad Sci 2014;126:1417-22.
19. Natarajan S, Mahata P, Sarma D. The relevance of metal organic frameworks (MOFs) in inorganic materials chemistry. Indian Acad Sci 2012;124:339-53.
20. Nfor EN, Keenan LL, Nenwa J, Ndifon PT, Njong RN, Dzesse CN, *et al*. A novel mixed ligand dinuclear complex of Co(II): Synthesis, characterization and magnetic studies. Cryst Struct Theory Appl 2014;3:22-9.
21. Shinde KN, Dhobe SJ, Swart HC, Park K. Phosphate phosphors for solid-state lighting. Springer Ser Mater Sci 2012;174:41-6.